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PROCESS FOR STABILIZING CHLORINE DIOXIDE SOLUTION

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The present invention relates to compositions contain-
ing chlorine dioxide, useful as disinfecting, cleaning and
bleaching agents, etc. and to methods for making the
same; more particularly it relates to novel stabilized solu-
tions of chlorine dioxide and methods for making the
same.

Chlorine dioxide, which is normally a gas, is a well
known germicide, as well as a disinfecting, cleaning and
bleaching agent.

For most applications, it is not practical to use the
gaseous chlorine dioxide as such for a number of reasons.
Therefore, it is available and used in aqueous solution.
One method of making such solution is to bubble the
gaseous chlorine dioxide through water to produce a
saturated chlorine dioxide solution. A serious problem
with such solutions is that only a relatively small amount
of the chlorine dioxide gas remains in solution after
preparation thereof, such amount being too small for practical
purposes except for water purification. The reasons
for this are (1) the amount of chlorine dioxide capable
of being dissolved is small and (2) upon standing the
chlorine dioxide, except for small amounts, is given off.
Put in another way, chlorine dioxide solutions per se
which are sufficiently concentrated for most purposes are
too unstable. Sodium perborate has been used to increase
the concentration of chlorine dioxide which can be placed
in stable solution, the chlorine dioxide being bubbled into
water containing sodium perborate.

However, there has been a need to further increase
the stable chlorine dioxide concentration, one reason being
reduction of shipping costs and another being the desirability
of providing stronger solutions for certain purposes.

It is an object of the present invention to fill this need,
i.e. to increase the stable chlorine dioxide concentration
in aqueous solutions thereof.

It has been discovered that the use of alkali metal
(sodium) percarbonate instead of sodium perborate in-
creases the amount of chlorine dioxide which can be
held in stable solution as much as three hundred percent.
It is believed that the sodium percarbonate becomes
chemically bonded in some way through the peroxy
radical to the chlorine dioxide to thereby hold the
chlorine dioxide in solution until it comes into contact
with a media which changes the pH factor during use
upon which the chlorine dioxide is released. In any
event, tests have proved that the chlorine dioxide is not
present in the form of a chlorite or chlorous acid. Prefer-
ably, an amount of sodium percarbonate is used which
will produce a saturated solution thereof in the final prod-
uct. In practice, about two parts by weight of percar-
bonate for each part of chlorine dioxide has been found
to provide optimum stable ClO_2 concentrations. If lesser
amounts are used, stability of the same chlorine dioxide
concentration is decreased. However, such lesser amounts
provide stable solutions of lesser ClO_2 concentrations.

Example 1

17 lbs. of chlorine dioxide were bubbled into 90 gal-
lons of water at room temperature while adding 100 lbs.
of sodium perborate. The chlorine dioxide concentra-
tion was 2% based on total weight of the resulting mix.
The ClO_2 concentration did not decrease upon standing

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for a period of five months. Increasing the amount of
chlorine dioxide did not result in any increase in solu-
tion concentration. Instead, the excess chlorine dioxide
escaped from the solution. Adjustment of the amount
of perborate did not increase the maximum ClO_2 con-
centration.

Example 2

50 lbs. of chlorine dioxide were bubbled into 90 gal-
lons of water at room temperature over a period of
twenty four hours while adding 100 lbs. of sodium per-
carbonate containing 70% by weight carbonate and 30%
hydrogen peroxide. The chlorine dioxide concentration
was 6% by weight of the resulting mix and did not de-
crease upon standing for a period of five months. In-
creasing the amount of chlorine dioxide did not result
in any increase in solution concentration. Instead the
excess chlorine dioxide escaped from the solution. Ad-
justment of the amount of percarbonate did not appre-
ciably increase the maximum chlorine dioxide concentra-
tion.

Although the use of percarbonate substantially in-
creases the maximum stable chlorine dioxide concentra-
tion, the cost of the product, even though less than with
the use of perborate because of increased ClO_2 concentra-
tion, is still relatively high because of the high cost of
percarbonate. It is an object of the present invention to
produce stable chlorine dioxide solutions of concentra-
tions at least as high as those achieved with percarbonate
at only a fraction, as little as about 1/4 of the cost and
to produce such solutions with other materials.

This is achieved by virtue of the discovery that it is
the active oxygen of the hydrogen peroxide of the per-
carbonate in combination with the carbonate thereof
which increases the stable ClO_2 concentration and that
substantially less (50% less) active oxygen is required
to do this than is present in the percarbonate containing
the necessary amount of carbonate. Thus, with percar-
bonate, of necessity, twice as much hydrogen peroxide is
being used than is necessary to stabilize the chlorine di-
oxide. Therefore, by using an alkali metal (sodium) car-
bonate or bicarbonate (both are inexpensive) and a
metered quantity of hydrogen peroxide, or some other
source of active oxygen such as ozone, substantially less
than the quantity present in percarbonate containing the
same amount of carbonate, the same stable concentra-
tion of chlorine dioxide can be achieved at only a fraction
(about 1/4) of the cost using the relatively expensive
percarbonate.

The present invention also contemplates using the ex-
cess peroxide or active oxygen in the percarbonate by
addition of sodium carbonate or bicarbonate to the per-
carbonate in sufficient amount to utilize all the available
active oxygen.

Although it is believed that the active oxygen of the
hydrogen peroxide, added as such or present in the per-
carbonate, causes the chlorine dioxide to become bound
in some way to carbonate or bicarbonate to thereby hold
it in solution, the resulting composition does not contain
any hydrogen peroxide or active oxygen.

Commercially available sodium percarbonate, e.g. that
sold by Food Machinery Company, contains seventy per-
cent by weight sodium carbonate and 30% hydrogen
peroxide. Of the 30% hydrogen peroxide about 47%
by weight is active oxygen so that the percarbonate con-
tains about 14% of active oxygen and 70% carbonate.
However, only about half of this amount of active oxygen
is required for the amount of sodium carbonate present
in the percarbonate for optimum stable ClO_2 concentra-
tions so that about 7% active oxygen or 15% hydrogen
peroxide, is being wasted. Not only does this result in
a waste of the hydrogen peroxide but the cost of combin-